

## Interaction of a poly(acrylic acid) oligomer with dimyristoylphosphatidylcholine bilayers

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### Abstract

We studied the influence of 5 kDa poly(acrylic acid) (PAA) on the phase state, thermal properties, and lateral diffusion in bilayered systems of dimyristoylphosphatidylcholine (DMPC) using  $^{31}\text{P}$  NMR spectroscopy, differential scanning calorimetry (DSC),  $^1\text{H}$  NMR with a pulsed field gradient, and  $^1\text{H}$  nuclear Overhauser enhancement spectroscopy (NOESY). The presence of PAA does not change the lamellar structure of the system.  $^1\text{H}$  MAS NOESY cross-peaks observed for the interaction between lipid headgroups and polyion protons demonstrated only surface PAA-biomembrane interaction. Small concentrations of PAA (up to  $\sim 4$  mol %) lead to the appearance of a new lateral phase with a higher main transition temperature, a lower cooperativity, and a lower enthalpy of transition. Higher concentrations lead to the disappearance of measurable thermal effects. The lateral diffusion coefficient of DMPC and the apparent activation energy of diffusion gradually decreased at PAA concentrations up to around 4 mol %. The observed effects were explained by the formation of at least two types of PAA-DMPC lateral complexes as has been described earlier (Fujiwara, M.; Grubbs, R. H.; Baldeschwieler, J. D. J. *Colloid Interface Sci.*, 1997, 185, 210). The first one is characterized by a stoichiometry of around 28 lipids per polymer, which corresponds to the adsorption of the entire PAA molecule onto the membrane. Lipid molecules of the complex are exchanged with the "pure" lipid bilayer, with the lifetime of the complex being less than 0.1 s. The second type of DMPC-PAA complex is characterized by a stoichiometry of 6 to 7 lipids per polymer and contains PAA molecules that are only partially adsorbed onto the membrane. A decrease in the DMPC diffusion coefficient and activation energy for diffusion in the presence of PAA was explained by the formation of a new cooperative unit for diffusion, which contains the PAA molecule and several molecules of lipids. © 2011 American Chemical Society.

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